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Structure of the solubility diagram in the Na_2SO_4-Na_2CO_3-$NaHCO_3$-H_2O system AT 0, 25 and 50 °C

The solubilities in invariant points of Na_2SO_4-Na_2CO_3-$NaHCO_3$-H_2O system were investigated at 0, 25 and 50 °C. The phase equilibria in the said system were discussed, and phase diagrams at given temperatures were constructed.

Keywords: solubility, phase equilibria, liquid phase, chemical analysis, crystallo-optical analysis, phase diagram

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Introduction

Four-component system Na_2SO_4-Na_2CO_3-$NaHCO_3$-H_2O is a part of more complex six-component system Na, Ca// SO_4, CO_3, HCO_3, F-H_2O. Equilibria in the latter determine the conditions of aluminium production liquid waste disposal. The waste water of cryolite recycling plants contains fluorides, carbonates, bicarbonates and sulphates of sodium and calcium [1, 2]. Crystallization and dissolution processes in such waste water are governed by the phase equilibria both in six-component system Na, Ca//SO_4, CO_3, HCO_3, F-H_2O and in its constituents, five- and four-component systems.

In our earlier studies [3, 4] the phase diagrams in similar systems were constructed. This study presents the results of investigation of Na_2SO_4-Na_2CO_3-$NaHCO_3$-H_2O system at 0, 25 and 50 °C using solubility method. The main goal of this work was to establish the concentration parameters of geometrical images and separation of the crystallization fields of individual equilibrium solids in the phase diagrams.

Results and discussion

The system investigated contains the following equilibrium solid phases: Nk – nahcolite $NaHCO_3$ (0, 25, 50 °C); Mb – mirabilite $Na_2SO_4 \cdot 10H_2O$, C·10 – $Na_2CO_3 \cdot 10H_2O$ (0, 25 °C); Tr – throne $NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O$ (25, 50 °C); Th – thenardite Na_2SO_4, Bur – burkeite $2Na_2SO_4 \cdot Na_2CO_3$, C·1 – $Na_2CO_3 \cdot H_2O$ (50 °C) [5, 6].

The following reagents were used in xperiments: $Na_2SO_4 \cdot 10H_2O$ ("chemically pure" grade), Na_2CO_3 ("pure" grade), $NaHCO_3$ ("pure" grade). The xperiments were carried out according to "saturation method" described in detail elsewhere [8].

Based on the data available [5, 6], we prepared the mixtures of precipitates with saturated solutions according to the invari-

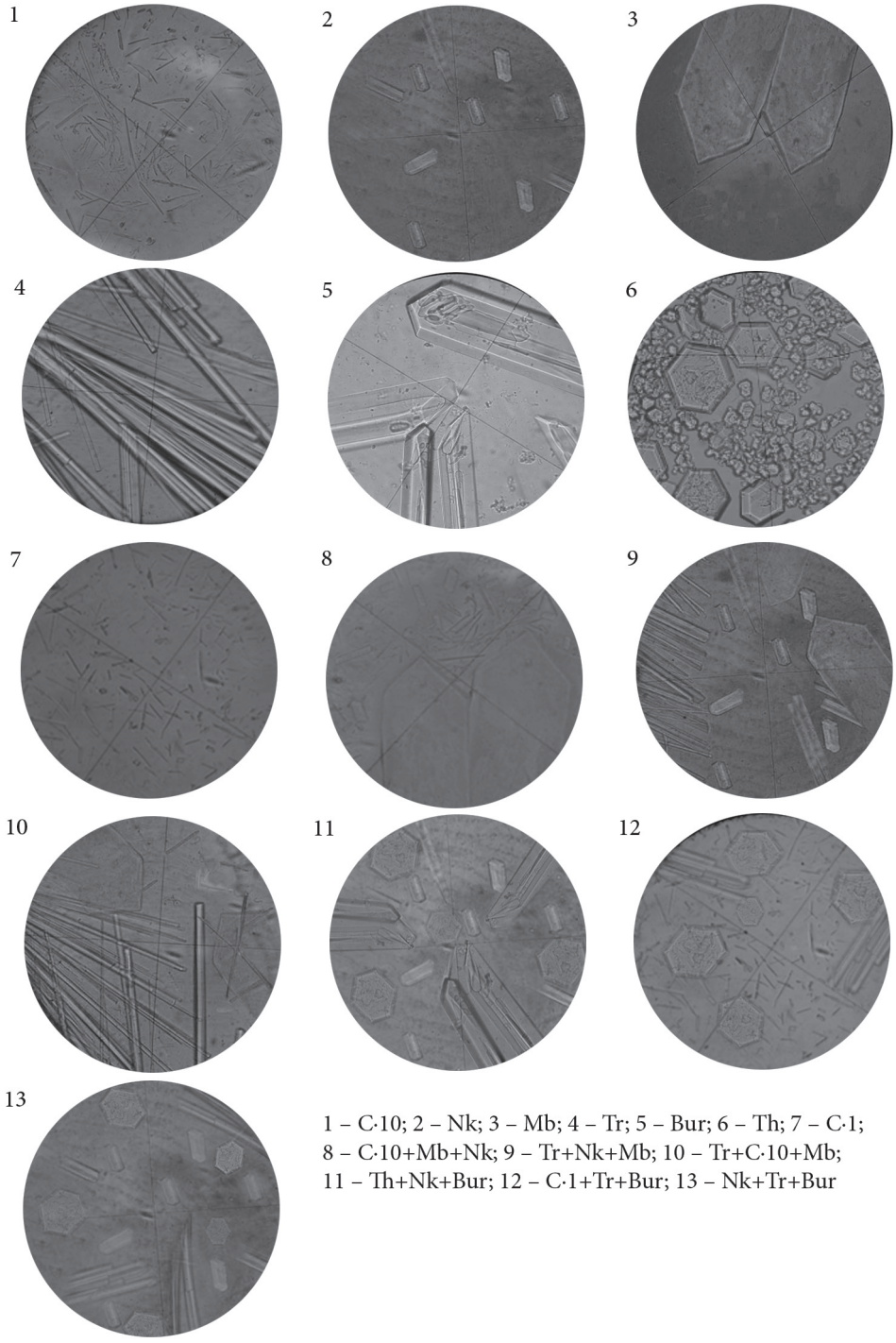

Fig. 1. Micrographs of equilibrium solid phases, corresponding to the invariant points of system Na_2SO_4-Na_2CO_3-$NaHCO_3$-H_2O at 0 (1, 2, 3, 8), 25 (1, 2, 3, 4, 9, 10) and 50 (2, 4, 5, 6, 7, 11, 12, 13) °C

ant points in the three-component systems Na_2SO_4-Na_2CO_3-H_2O, Na_2SO_4-$NaHCO_3$-H_2O and Na_2CO_3-$NaHCO_3$-H_2O at 0, 25 and 50 °C. Then, transferring the non-variant points from the three-component section to the four-component section [3, 4], the saturated solutions prepared had been kept in a thermostat at a given temperature until the equilibrium was reached.

Thermostating was carried out in U-8 ultra-thermostat. Stirring was performed using a PD-09 magnetic stirrer for 50–120 h. Temperature was maintained with 0.1 °C accuracy using a contact thermometer. Crystallization of solid phases was observed with a POLAM-R 311 microscope. After the equilibrium in a given system was achieved, the solid phases were photographed with a Sony-DSC-S500 digital camera. Equilibrium was assumed to be attained when the phase composition of the precipitates was constant.

A Buchner funnel with an ash-free filter paper (Blue Band) connected to a vacuum pump has been used for separation of the liquid phase and solid phase. The precipitate after filtration was washed with 96% ethanol and then dried at 120 °C. The

Table 1

Solubility in central (invariant) points in system Na_2SO_4-Na_2CO_3-$NaHCO_3$-H_2O

№ of points	Structure of a liquid phase, mas. %				Phase composition of deposits
	Na_2SO_4	Na_2CO_3	$NaHCO_3$	H_2O	
0 °C					
E_1^3	2.73	–	5.58	91.69	Mb+Nk
E_2^3	–	5.6	4.6	89.8	Nk+ C·10
E_3^3	2.8	6.0	–	91.2	C·10+Mb
E_1^4	2.12	5.13	4.37	88.38	Mb+Nk+C·10
25 °C					
E_1^3	16.4	18.3	–	65.3	Mb+C·10
E_2^3	20.68	–	4.16	75.16	Nk+Mb
E_3^3	–	17.62	4.62	77.76	Tr+Nk
E_4^3	–	22.46	2.84	74.7	C·10+Tr
E_1^4	21.2	20.07	5.51	50.22	Mb+Tr+C·10
E_2^4	20.9	22.54	4.77	50.68	Nk+Tr+Mb
50 °C					
E_1^3	29.65	–	4.05	66.30	Th+Nk
E_2^3	22.47	10.52	–	67.61	Th+Bur
E_3^3	5.87	28.52	–	65.61	Bur+C·1
E_4^3	–	16.92	6.30	76.78	Nk+Tr
E_5^3	–	31.80	0.85	67.35	Tr+C·1
E_1^4	12.64	21.31	2.51	54.76	Th+Nk+Bur
E_2^4	4.30	24.36	0.64	58.03	Bur+Tr+C·1
E_3^4	7.52	9.14	3.24	60.08	Tr+Nk+Bur

standard techniques used for the chemical analysis of products are described elsewhere [8–10].

Results of the crystallooptical analysis [11] of equilibrium solid phases (microphoto) are presented in Fig. 1, and the results of the chemical analysis of the saturated solutions are given in Table 1.

On the basis of the data obtained, the diagrams of solubility in the Na_2SO_4-Na_2CO_3-$NaHCO_3$-H_2O system at 0, 25 and 50 °C were constructed. Salt parts of these diagrams are shown in Fig. 2. The location of non-variant points on the diagrams were determined by the center of mass method [12].

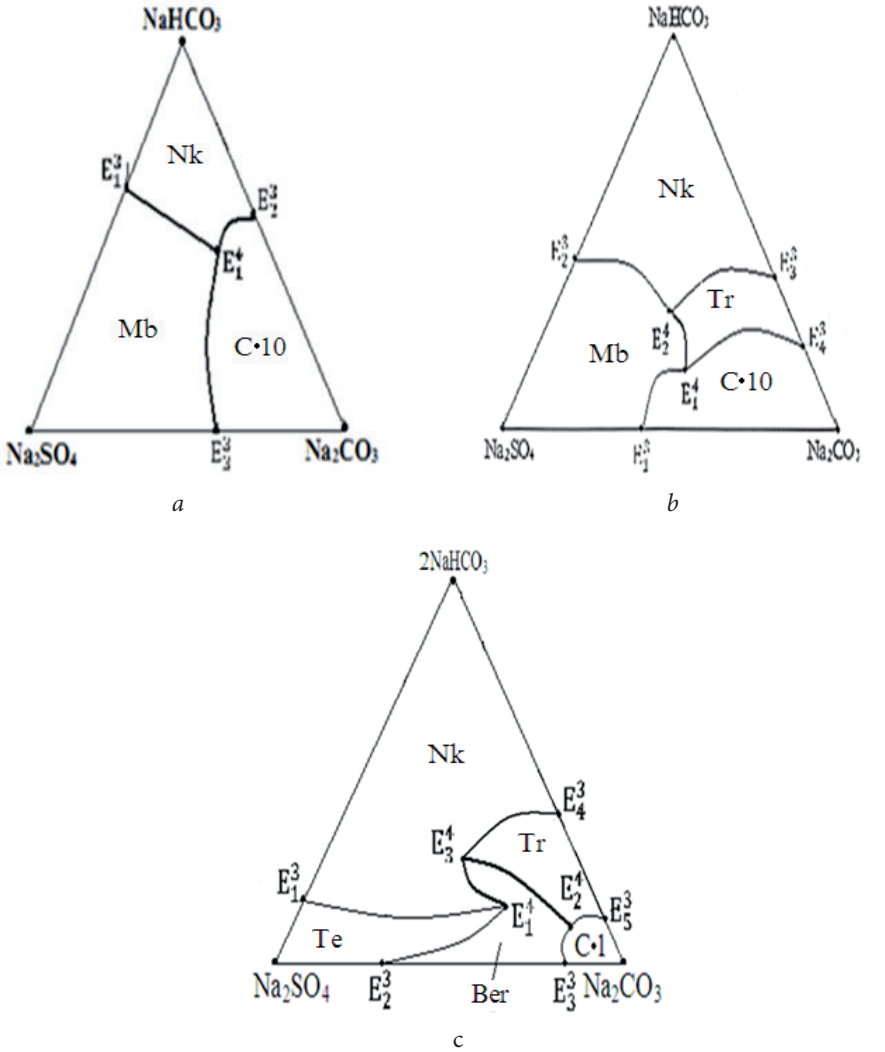

Fig. 2. Solubility diagrams in Na_2SO_4-Na_2CO_3- $NaHCO_3$-H_2O system:
a – at 0 °C; *b* – at 25 °C; *c* – at 50 °C

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